

Abstract No. dinn221

The First Crystallographic Proof of the Peroxodicarbonate Anion in $K_2[C_2O_6]$ from High Resolution Powder Diffraction Data

R. Dinnebier, S. Vensky, M. Jansen (MPI Stuttgart), P. Stephens (SUNY, Stony Brook)

Beamline: X3B1

Introduction: Although alkali peroxodicarbonates like $K_2[C_2O_6]$ have been synthesized as early as 1895¹, it seems to be impossible to grow single crystals suitable for X-ray structure determination allowing to crystallographically prove the existence of the peroxodicarbonate anion. High resolution powder diffraction techniques allow us to perform the first known structure determination of a peroxodicarbonate.

Methods and Materials: X-ray powder diffraction data for the extremely temperature and moisture sensitive compound were collected at $T = 200$ K using a closed cycle He-cryostat ($\lambda = 1.5015(2)$ Å) in transmission geometry with the sample sealed in a 0.7 mm lithiumborate glass capillary. Data reduction was performed using the GUF1 program. Indexing with ITO led to a monoclinic unit cell (space group $P2_1/c$ with lattice parameters of $a = 8.4073(2)$, $b = 10.7851(2)$, $c = 7.1481(2)$ Å, and $\beta = 111.399(8)^\circ$). The crystal structure was solved using the simulated annealing program DASH (CCDC) and refined by the GSAS Rietveld refinement package. Two additional phases were present in the powder pattern from which potassium hydrogencarbonate (kalcinite) was also included in the Rietveld refinement.

Results: $K_2[C_2O_6]$ exhibits a framework structure of irregular KO_7 polyhedra which can be derived from strongly distorted octahedra resp. trigonal prisms with an additional oxygen atom on top of one of their faces (Fig. 1). All corners of the potassium polyhedra are linked to carbonate groups. The crystal structure could be refined freely, establishing the peroxodicarbonate anion which has an oxygen-oxygen bond length of $1.47(1)$ Å, and a torsion of 93° (Fig. 2).

Acknowledgments: This work was supported by the Max-Planck-Society (MPG), the Fonds der chemischen Industrie (FCI) and the Division of Basic Energy Sciences, U.S. DOE (DE-FG02-86ER45231).

References: E. J. Constan, A. von Hansen, Zeitschrift für Elektrochemie 7, (1895)¹

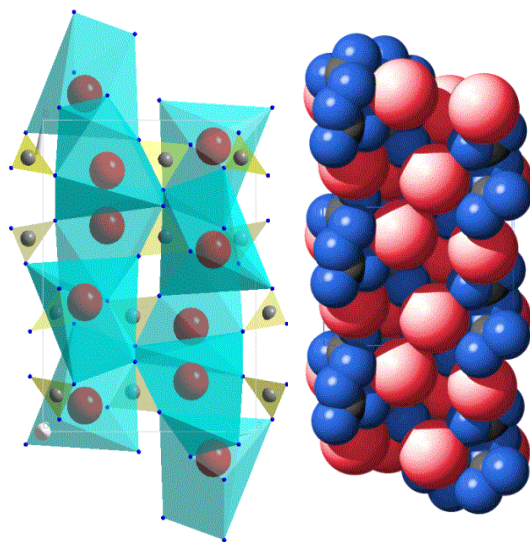
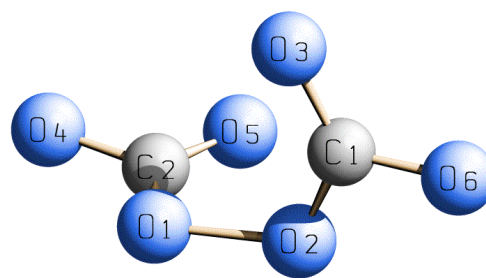


Figure 1. Two views of the crystal structure of $K_2[C_2O_6]$ at $T = 200$ K in a projection along c -axis.



SCHAKAL

Figure 2. Twisted (93°) peroxodicarbonate anion in the crystal structure of $K_2[C_2O_6]$ at $T = 200$ K.